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THE VAPOR PRESSURE OF ARSENIC TRIOXIDE

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ENGIN STORAGE

BY

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AND

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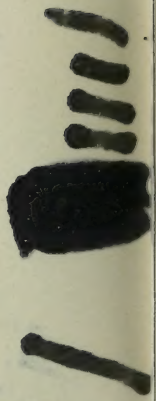

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THE VAPOR PRESSURE OF ARSENIC TRIOXIDE.

By H. V. Welch and L. H. Duschak.

INTRODUCTION.

Among the investigations being conducted by the Bureau of Mines with reference to the increase of safety and efficiency in the mineral industries are those relating to metallurgical smoke, especially the smoke from plants for roasting or smelting sulphide ores. The bureau is investigating the conditions that render such smoke injurious to animal and vegetable life, the methods by which the injurious effects can be lessened, the recovery of valuable substances from the smoke, and the possibility of finding new uses for substances that now are wasted in the smoke because of the lack of a market. Early in the course of its investigations the bureau found that more information than was available in the literature was needed concerning the physical and chemical properties of various substances present in smelter smoke as gas or fume.

The work described in this report was begun in the chemical laboratory of the University of California by H. V. Welch, at the suggestion of F. G. Cottrell, then assistant professor of physical chemistry at the university, and was completed at the San Francisco experiment station of the Bureau of Mines.

THE ARSENIC PROBLEM IN SMELTING.

One of the most deleterious substances in the smoke from many metallurgical plants is arsenic. The important sulphide ores of lead, copper, and other common metals contain appreciable and often considerable proportions of arsenic. In the usual metallurgical treatment of these ores part of the arsenic collects in flues or settling chambers as impure arsenic trioxide, which is subsequently purified by sublimation.[a] The increasing regard in this country for a more complete recovery of this substance arises not only from the necessity of avoiding air pollution in certain regions, but also from the growing interest of the smelting companies in greater recovery and utilization of by-products. The recovery of arsenic trioxide contained in the

[a] See Dunn, E. M., Determination of gases in smelter flues; and note on the determination of dust losses at the Washoe reduction works, Anaconda, Mont.: Bull. Am. Inst. Min. Eng., vol. 46, August, 1913, p. 2069.

hot flue gases involves two distinct processes—first, the condensation of the vapor by cooling; and, second, the separation of the minute solid particles, or so-called "fume," from the true gases. The second process is purely mechanical, and can now be successfully handled in several different ways; but as much, unfortunately, can not be said of the first process.

PURPOSE OF INVESTIGATION.

For the proper designing and control of equipment for the condensation of arsenic trioxide vapor a knowledge of the vapor pressure of the substance is required. A few determinations of this constant have been made by Stelzner[a] and by Niederschulte[b] at temperatures somewhat higher than those particularly important as regards fume control in metallurgical work. Aside from these measurements, the authors of this paper have found no data on the subject, and they undertook the work here described not only to obtain information concerning arsenic trioxide, but also with the idea of developing a convenient apparatus for the examination of other slightly volatile solids.

EXPERIMENTAL PROCEDURE.

METHOD AND APPARATUS.

The so-called air-saturation method was employed,[c] the experiment consisting in determining the weight of substance necessary to saturate a given volume of air under given conditions of temperature and pressure. The principal parts of the apparatus are shown in figure 1, in Plate I, *A* and *B*, and the entire equipment in Plate II, *A*.

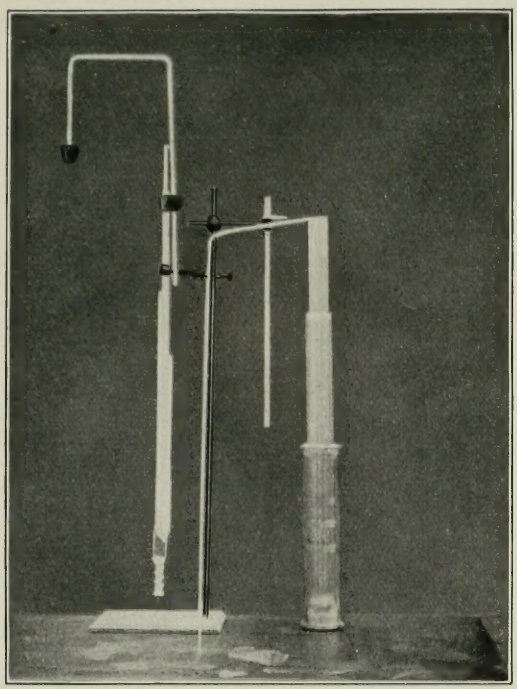
The material under investigation was contained in the annular space between tubes *a* and *b* (fig. 1). Air passed down the outer tube through the material and out through tube *c*, which fitted snugly within tube *b* and served as a condenser. A plug of glass wool at the bottom of tube *a* prevented the transportation of solid particles by the stream of air. At the close of an experiment, tube *c* was easily removed for the determination of the condensed material without otherwise disturbing the apparatus. The side tube on tube *d* was connected to an aspirator, so that a stream of air in addition to that flowing through *c* was drawn through tube *a;* this stream of air cooled the upper parts of tubes *a*, *b*, and *c*, assisted in condensing the arsenic trioxide vapor in tube *c*, and was particularly useful in avoiding overheating.

---

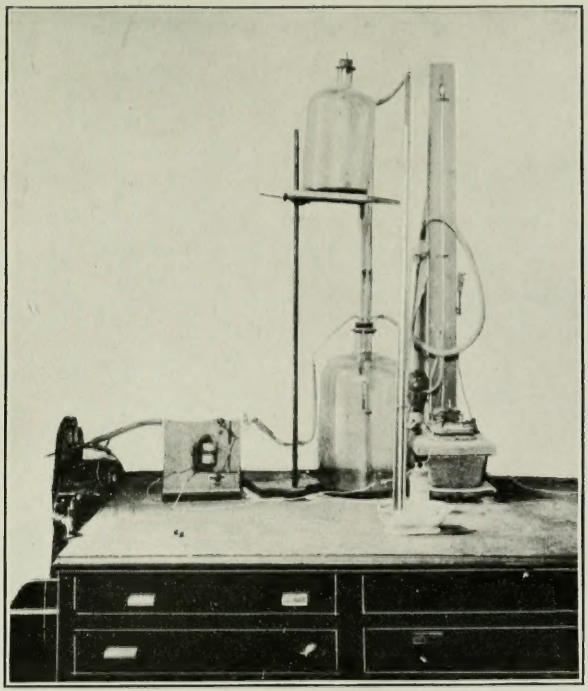
a Stelzner, Karl, Über den Dampfdruck fester Körper. Dissertation, Erlangen University, 1901.

b Niederschulte, Gustav, Über den Dampfdruck fester Körper. Dissertation, Erlangen University, 1903.

c This method is based on experiments of Regnault and Magnus. See Walker, J., Über eine Methode zur Bestimmung der Dampfspannungen bei neideren Temperaturen: Zeitschr. phys. Chem., Bd. 2, 1888, p. 602; Will, W. and Bredig, G., Einfache Moleculargewichtsbestimmung gelöster Substanzen: Ber. Deutsch. Chem. Gesell., Jahrg. 22, 1889, p. 1084; and Stelzner, Karl, and Niederschulte, Gustav, loc. cit.



A. AIR-SATURATING APPARATUS AND VAPOR BATH, SHOWING PARTS.



B. APPARATUS FOR AUTOMATIC REGULATION OF PRESSURE IN VAPOR BATH.

THERMOSTAT.

Constant temperatures between 120° and 215° C. were obtained by immersing the apparatus in a vapor bath. Brombenzol, aniline, and methyl salicylate were employed, the pressure above the liquid being adjusted according to the tables of Ramsey and Young [a] to insure the desired temperature.

The liquid was heated internally by a spiral of platinum-iridium wire of about 10 ohms resistance wound on a glass bobbin, a current of 1.2 to 1.5 amperes being used. An early difficulty from superheating was largely overcome by the use of the glass jacket *e* (fig. 1) and by the internal air cooling of the upper part of tube *b*. With this arrangement the bath vapor was condensed on the cooled upper part of tube *b*, so that its lower part as well as the inside of the vapor jacket *e* was covered with a film of returning liquid. Under these conditions trouble from superheating was very greatly reduced but not entirely eliminated in all experiments. As a control, a calibrated thermometer was attached to tube *a* and observed at intervals during each experiment. In most cases the temperature indicated by the thermometer differed by only a few tenths of a degree from that given in the boiling-point table of Ramsey and Young. Occasionally a divergence of as much as 1° was noted. The vapor bath was surrounded by two concentric glass cylinders, which served as protecting jackets and supports for the apparatus.

Regulation of pressure in the vapor bath was obtained by the apparatus shown in Plate I, *B*. Tube *f* (fig. 1) from the top of the vapor bath was joined through the upper bottle (Pl. I, *B*) to the 12-liter bottle below, which in turn was connected to an aspirator,

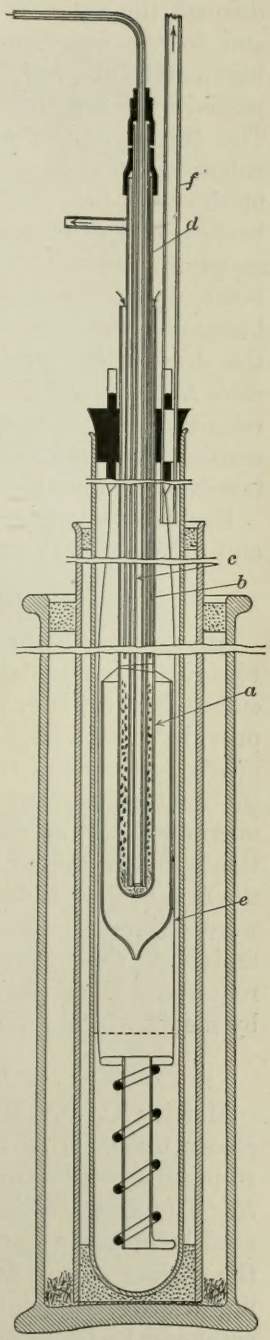


FIGURE 1.—Cross section of air-saturating apparatus and vapor bath.

[a] Ramsey, W., and Young, S., A method for obtaining constant temperature: Jour. Chem. Soc., vol. 47, 1885, p. 640. Brombenzol—pressure, 279.9 to 766.7 mm.; temperature, 120° to 157° C.; aniline—pressure, 283.7 to 771.5 mm.; temperature, 150° to 185° C.; methyl salicylate—pressure, 228.3 to 779.8 mm.; temperature, 177° to 224° C.

through the valve at the left, to the manometer in the foreground, and to the open end of the barometer tube at the right. This barometer tube had a movable reservoir suspended by a cord that passed over a pulley and was attached to a fine adjustment screw. The tube was provided with two platinum contacts, one in the enlargement at the top and the other connecting with the mercury in the tube below. These contacts were in circuit with a suitable battery and a telegraph relay which in turn controlled the current supplying the electrically actuated valve. When the pressure in the bottle increased sufficiently, electrical contact at the top of the barometer tube closed the relay circuit and sent a current through the electromagnet by which the valve was opened. When the aspirator had reduced the pressure to the desired point the contact broke, releasing the valve which automatically closed. The pressure was accurately determined with the manometer, and by careful adjustment it was easily possible to reduce the variations to less than 0.5 mm.

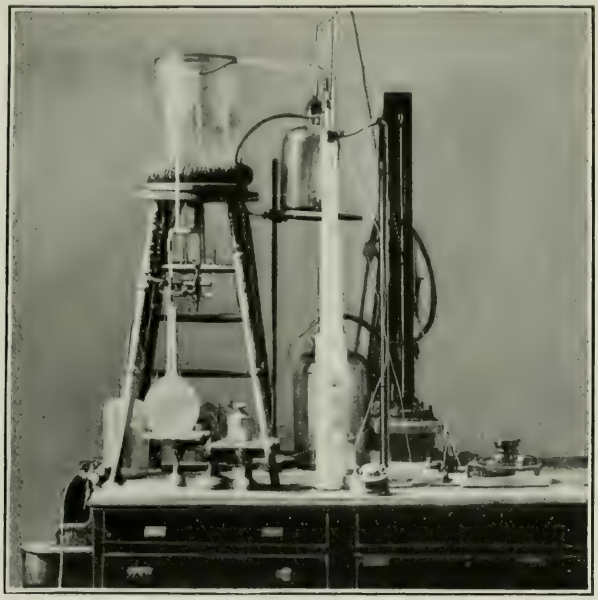
For determinations at 100° C. water was used in the vapor bath and tube *f* (fig. 1) was replaced by a reflux condenser.

MEASUREMENT OF AIR VOLUMES.

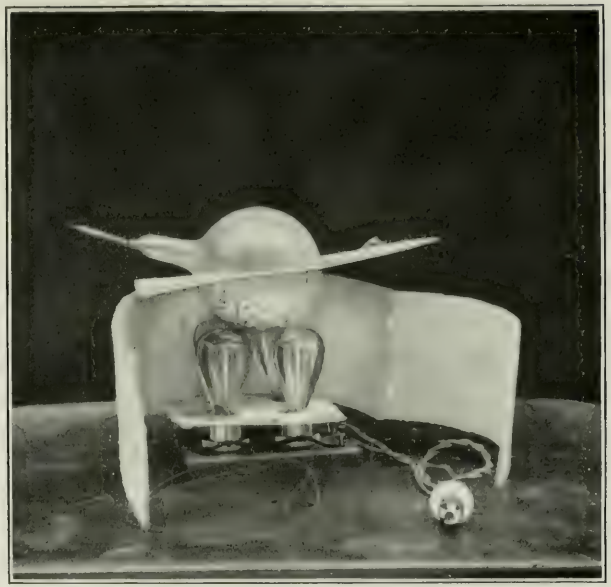
Air was drawn through the apparatus by the aspirator shown in Plate II, *A*, at the left. The water flowing from the large bottle was collected in a 2-liter graduated flask mounted on a balance that was provided with a trigger device, so that when the flask had been filled nearly to the mark the flow of water was automatically interrupted, the final adjustment to exactly 2 liters being made by hand. The maximum rate at which air might be passed with complete saturation was determined by a series of preliminary experiments in which the rate of flow was increased until low values for the vapor pressure were obtained. The rates employed were always well within the limit. At the lower temperatures at which a large volume of air was required a small gas meter was used. This was frequently calibrated by means of the aspirator and a graduated flask.

PREPARATION OF MATERIAL.

Merck's C. P. arsenic trioxide was fused and then frozen as a glassy mass. This mass was crushed and the part retained on a 10-mesh screen was sublimated in the apparatus shown in Plate II, *B*. The flask was heated by four 32-candlepower bulbs and evacuated in order to remove all moisture. The final evacuation, before the sealing of the flask, was completed by the use of charcoal and liquid air. In about a month a fine crop of large crystals (regular octahedra) had formed on the cool upper surface of the flask. Only the coarser parts of this material retained on a 10-mesh screen were used for charging the vapor-pressure apparatus, thus reducing to a minimum the resistances offered to the passage of the air.



A. APPARATUS ASSEMBLED FOR MAKING TEST.



B. APPARATUS FOR SUBLIMING ARSENIC TRIOXIDE.

DETERMINATION OF ARSENIC TRIOXIDE SUBLIMED.

At the close of an experiment, the tube *c* (fig. 1) was removed and the arsenic trioxide condensed within, often in the form of brilliant crystals, was dissolved by a small quantity of sodium hydroxide solution. The solution was then neutralized with dilute hydrochloric acid and the arseneous acid determined by the use of standard iodine solution following the method outlined in Sutton's "Volumetric Analysis." A tenth or a hundredth normal iodine solution was used according to the quantity of arseneous acid to be determined, and the iodine solutions were standardized by comparisons with standard solutions prepared from some of the same arsenic trioxide used for the vapor-pressure determinations.

CALCULATION OF VAPOR PRESSURE.

It became evident early in the work that because of the many factors involved a high degree of accuracy for each experiment was not to be expected. A considerable number of determinations were therefore made at each temperature.

The value of the vapor pressure for each experiment was computed as follows:

If V represented the volume of air passed reduced to standard conditions, and v represented the hypothetical volume occupied by the arsenic trioxide vapor under standard conditions, then the vapor pressure in millimeters would equal $760 \times \frac{v}{V+v}$. For most experiments, the value of v is so small in comparison with that of V that the expression becomes simply $760 \times \frac{v}{V}$.

In computing V from the volume of water displaced from the aspirator the average temperature and pressure for the entire series were employed instead of the mean during each experiment. These averages computed from a large number of observations were as follows:

	Mean.	Maximum observed.	Minimum observed.
Pressure, mm	758.9	763.4	753.2
Temperature, ° C.	14	17	11

It was further assumed that the air entering the apparatus was saturated with water vapor. This assumption was not far from the truth as a large open thermostat maintained at 25° C. stood in the same room near the apparatus. The errors introduced by these simplifications are well within the other experimental errors.

In calculating v from the weights of the arsenic trioxide recovered the molecular weight was taken as 396, corresponding to a formula As_4O_6,[a] and it was assumed that the vapor obeyed the gas laws.

RESULTS OBTAINED.

The results of all the experiments carried to a successful conclusion are recorded in Table 1. The first column gives the serial number of the experiment; the second, the mean temperature; the third, the volume of air passed, measured at room conditions; the fourth, the weight in grams of As_2O_3 recovered from tube *c;* and the fifth, the vapor pressure, expressed in millimeters of mercury.

TABLE 1.—*Summary of experimental results.*

No.	Mean temperature.	Volume of air.	As_2O_3 sublimed.	Vapor pressure.	No.	Mean temperature.	Volume of air.	As_2O_3 sublimed.	Vapor pressure.
	°C.	Liters.	Grams.	Mm.		°C.	Liters.	Grams.	Mm.
1	178.1	2	0.00737	0.167	56	210.5	2	.0574	1.296
2	177.9	2	.00763	.172	57	210.3	2	.0458	1.036
3	180.0	2	.00878	.198	58	210.7	2	.0494	1.117
4	176.6	2	.00757	.171	59	209.0	2	.0491	1.111
5	176.5	2	.00772	.174	60	214.0	2	.0681	1.54
8	178.1	2	.00755	.171	61	214.3	2	.0666	1.50
9	177.8	2	.00767	.173	62	214.6	2	.0688	1.55
10	177.1	2	.00817	.185	64[b]	262.5	2	.600	13.4
11	177.4	2	.00768	.174	65[b]	266.7	2	.636	14.1
12	181.1	2	.00814	.184	66	100.0	560	.00327	.000264
13	180.2	2	.00799	.181	67	171.1	2	.00374	.0845
14	181.1	2	.00807	.182	68	172.0	2	.00451	.102
15	181.2	2	.00797	.180	69	168.7	2	.00299	.0674
16	181.0	2	.00811	.183	70	165.6	2	.00270	.0610
17	180.2	2	.00780	.176	71	164.9	2	.00258	.0583
18	179.7	2	.00838	.189	72	164.9	2	.00228	.0515
19	179.2	2	.00797	.180	73	159.7	2	.00166	.0375
20	179.3	2	.00980	.222	74	160.2	2	.00210	.0475
21	179.1	2	.00883	.200	75	159.5	2	.00200	.0452
22	179.1	2	.00877	.198	76	159.6	2	.00214	.0483
23	171.3	2	.00528	.119	77	155.5	2	.00168	.0380
24	172.7	2	.00561	.127	78	155.0	2	.00176	.0398
25	170.3	2	.00528	.119	79	154.0	2	.00170	.0384
26	184.5	2	.0119	.269	80	151.0	2	.00108	.0244
27	184.5	2	.0116	.262	81	150.5	2	.000927	.0210
28	184.5	2	.0118	.266	82	149.8	5	.00284	.0214
29	184.7	2	.0119	.269	83	150.0	10	.00466	.0210
30	184.4	2	.0118	.266	84	150.0	18.91	.0136	.0314
31	184.4	2	.0128	.289	85	149.4	54.68	.0299	.0247
32	184.6	2	.0128	.289	86	149.3	21.05	.0122	.0262
33	190.0	2	.0155	.350	87	150.0	32.51	.0194	.0270
34	189.8	2	.0160	.362	88	149.1	48.95	.0238	.0220
36	190.4	2	.0163	.368	91	146.3	124.37	.0424	.0154
37	190.0	2	.0220	.496	92	143.5	106.81	.0334	.0141
40	195.5	2	.0240	.542	93	132.2	38.58	.00462	.00541
41	200.1	2	.0287	.649	94	133.9	118.56	.0160	.00610
42	201.6	2	.0316	.713	96	135.0	187.64	.0261	.00628
43	200.2	2	.0306	.691	97	133.2	100.45	.0130	.00587
44	199.4	2	.0293	.662	98	134.2	54.22	.00729	.00608
45	200.4	2	.0323	.730	100	140.1	142.74	.0408	.0129
46	206.0	2	.0464	1.049	101	143.9	119.19	.0397	.0150
47	207.0	2	.0460	1.040	103	144.2	42.22	.0129	.0138
48	211.0	2	.0554	1.253	104	144.0	45.03	.0133	.0133
49	210.1	2	.0484	1.094	105	125.7	114.40	.00636	.00252
50	208.9	2	.0508	1.147	106	124.9	98.64	.00530	.00243
51	206.2	2	.0412	.930	108	126.8	289.31	.0166	.00259
52	206.2	2	.0429	.970	109	100.0	674.3	.00383	.000257
53	206.0	2	.0439	.991	110	100.0	588.1	.00381	.000293
54	206.2	2	.0430	.971	111	100.0	1,094	.00608	.000251
55	205.0	2	.0411	.928					

[a] Ostwald, Wilhelm, The Principles of Inorganic Chemistry, 1899, p. 707.

[b] The liquid of the vapor bath (methyl salicylate) had partly decomposed when these experiments were made. The boiling point was not constant and the results are, therefore, only approximate.

CALCULATION OF AVERAGE VALUES FOR VAPOR PRESSURE.

The many observations shown above may be most readily combined by making use of the relationship expressed in the familiar equation of Clausius:

$$\frac{d \ln p}{dT} = \frac{Q}{RT^2} \tag{1}$$

in which $\ln p$ is the natural logarithm of the vapor pressure, T the absolute temperature, R the gas constant, and Q the heat of sublimation. If it be assumed that Q is independent of the temperature, the general integrand of this equation is

$$\ln p = -\frac{Q}{RT} + B \tag{2}$$

in which B is the constant of integration. From this it can be seen that if the logarithm (either natural or common) of the vapor pressure be plotted as a function of the reciprocal of the absolute temperature, a straight line will result. The above assumption in regard to Q, however, is in general not strictly true, and the extent to which the actual $\ln p$ and $\frac{1}{T}$ curve deviates from a straight line indicates roughly the degree of approximation involved. For the comparison of individual experiments and the determination of mean values, the advantage of this flat curve over the rapidly bending graph of the vapor-pressure and temperature diagram (see fig. 2) is obvious.

The curve obtained by plotting the common logarithm of p against $\frac{1}{T}$ is shown in Plate III. The small circles represent single determinations and the large circles the averages of a number of groups of values that fall so near together that they can not be plotted separately. The determinations of Stelzner and Niederschulte, given in Table 2 following, are also included in the plot.

In reducing his results Stelzner [a] made use of the Dupré-Rankins formula

$$\ln p = A - \frac{B}{T} - C \ln T$$

which is derived from the Clausius equation on the assumption that Q is a linear function of the temperature, the method of least squares being employed in computing the constants A, B, and C. This procedure is of doubtful advantage when applied to so few observations as were made by Stelzner.

[a] Stelzner, Karl, Über den Dampfdruck fester Körper. Dissertation, Erlangen University, 1901.

TABLE 2.—*Data of Stelzner and Niederschulte.*

Temperature.	Vapor pressure.	Temperature.	Vapor pressure.
° C.	*M m.*	° C.	*Mm.*
165	[a] 0.027	268.6	24.4
240.8	6.3	280.1	42.1
253.1	12.2	290.9	65.4
261.8	18.2	306.8	110.6

[a] Niederschulte, remaining values by Stelzner.

The values of the vapor pressure taken from the curve for a series of temperatures ranging from 100 to 300° C., at 20-degree intervals, are given in Table 3. The third column gives the quantity of arsenic trioxide required to saturate 1,000 cubic feet of gas (air) measured at standard conditions when raised to the temperature noted, the total pressure being 1 atmosphere.

TABLE 3.—*Mean values of the vapor pressure of As_2O_3.*

Temperature.	Vapor pressure.	As_2O_3 per 1,000 cubic feet of gas.	Temperature.	Vapor pressure.	As_2O_3 per 1,000 cubic feet of gas.
° C.	*Mm. of mercury.*	*Pounds.*	° C.	*Mm. of mercury.*	*Pounds.*
100	0.000266	0.000386	220	2.065	3.00
120	0.00180	0.00261	240	5.96	8.71
140	0.01035	0.0150	260	15.7	23.2
160	0.0473	0.0685	280	38.5	58.6
180	0.186	0.270	300	89.1	144
200	0.653	0.947			

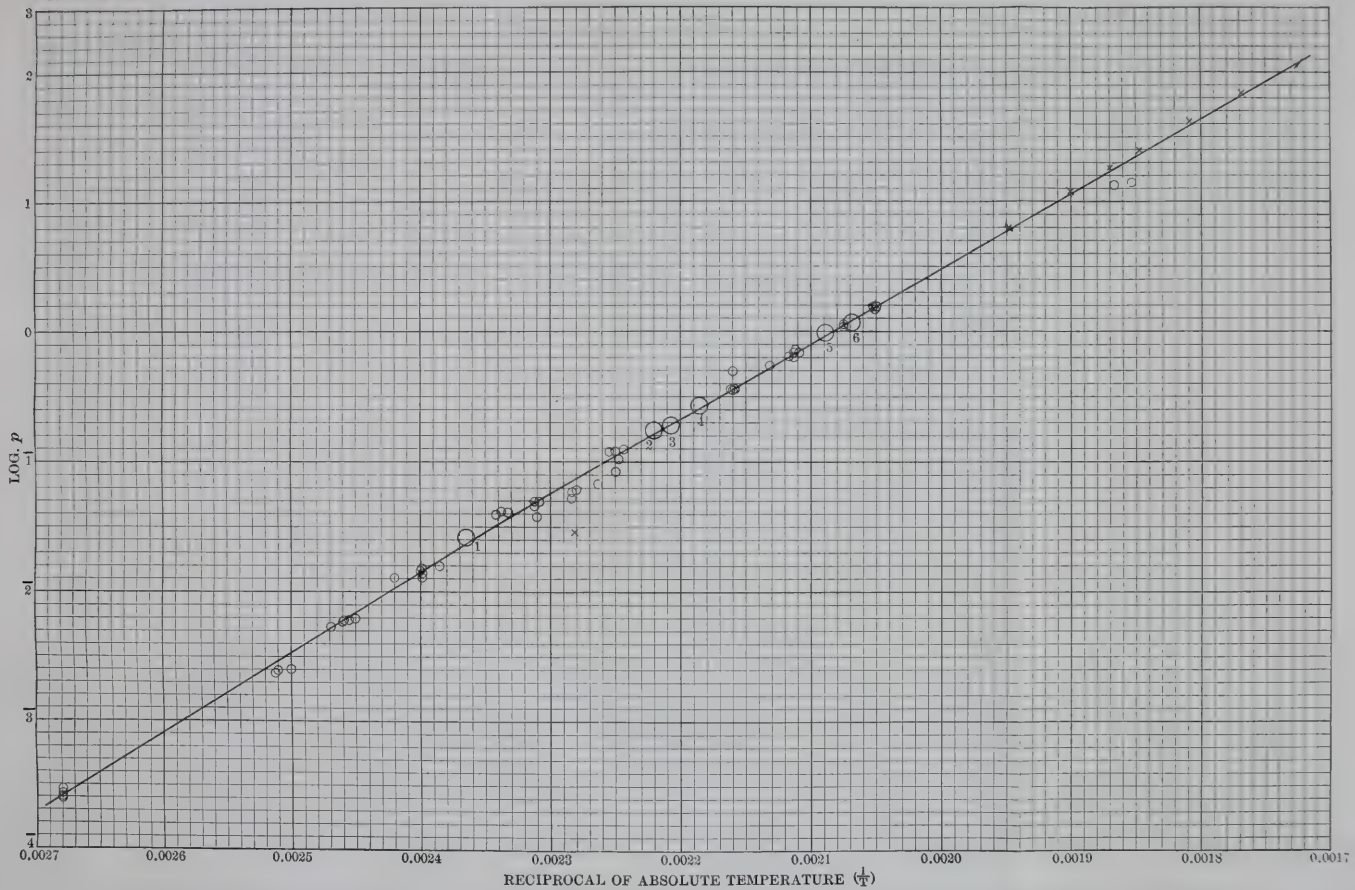
These values for the vapor pressure are believed to be accurate to about 1 per cent.

HEAT OF SUBLIMATION OF ARSENIC TRIOXIDE.

Equation 1 in integrated form may be expressed as follows:

$$\ln p_2 - \ln p_1 = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (3)$$

By using the equation as expressed above the heat of sublimation of arsenic trioxide may be calculated. When T_1 and T_2 are chosen so near together that the heat of sublimation is practically constant for the interval, Q represents the total heat absorbed when 1 gram molecule (in this case, 396 grams—see p. 10) vaporized at the temperature $\frac{T_1+T_2}{2}$. This quantity Q includes not only the so-called inner heat of sublimation, or change of internal energy ΔE, but also the external work performed by the evaporation of 1 gram molecule. If Δv represents the change in volume involved in this evaporation, then the external work is $p\Delta v = RT$, and then the relationship $Q = \Delta E + RT$ exists. The values of Q and ΔE calculated from the



CURVE SHOWING COMMON LOGARITHM OF VAPOR PRESSURE PLOTTED AS FUNCTION OF THE RECIPROCAL OF THE ABSOLUTE TEMPERATURE.

successive pairs of values for the vapor pressure given in Table 3 are shown in Table 4 below.

TABLE 4.—*Values of total and inner heats of sublimation of As_2O_3.*

Temperature.	Q.	E.	Temperature.	Q.	E.
° C.			° C.		
110	27930	27170	210	26610	25650
130	28040	27240	230	26650	25650
150	27210	26370	250	26340	25300
170	26710	25830	270	26240	25160
190	26750	25830	290	26500	25380

[a] Heat quantities are expressed in 15° gram-calories, the heat required to raise 1 gram of water from 14.5° C. to 15.5° C.

An inspection of the table shows that both Q and ΔE decrease with rising temperature, the latter, of course, more rapidly. From this direction of change of E one may conclude that the specific heat of solid arsenic trioxide and, at temperatures above 251° C., that of the subcooled liquid are greater than that of the vapor. The probable error in these heats of sublimation is the same as that in the vapor-pressure values employed, namely about 1 per cent.

CRYSTALLINE MODIFICATIONS OF ARSENIC TRIOXIDE.

FORMS—OCTAHEDRAL, MONOCLINIC.

Arsenic trioxide is known to occur in two crystalline forms—more commonly in octahedra as the mineral arsenolite, and less commonly in the monoclinic form found sparingly as claudetite. Also, an amorphous or glassy form is obtained by subcooling the substance from fusion. When arsenic trioxide is sublimed, either on a small scale in the laboratory or at the arsenic plant of a smelter in the usual refining process for crude arsenic, the product commonly shows octahedral crystallization. Sublimed arsenic trioxide in the octahedral form was accordingly used for the vapor-pressure determinations as representing the form to be considered in dealing with flue-dust problems. On completing the vapor-pressure measurements and the work on the vapor pressure of arsenic trioxide from flue dust described in this paper, it seemed worth while to consider more carefully the relationship between the various forms of arsenic trioxide.

INVESTIGATIONS BY OTHERS.

The monoclinic modification seems to have been first recognized by Wöhler,[a] and has been investigated by Debray,[b] Des Cloizeaux,[c] and others. The work of these chemists indicated that under cer-

[a] Wöhler, F., Ueber die Dimorphie der arsenigen Säure: Pogg. Ann., Bd. 26, 1832, p. 177.

[b] Debray, H., Sur le dimorphsme des acides arsénieux et antimonieux: Bull. Soc. chim. Paris, sér. 2, t. 2, 1864, pp. 9–11.

[c] Des Cloizeaux, —, Note sur la forme clinorhombique et les charactères optiques de l'acide arsénieux prismatique: Compt. rend., t. 105, 1887, p. 96.

tain conditions the monoclinic form may be obtained by condensing arsenic trioxide vapor at a temperature above 200° C. or by prolonged heating at or above 100° C. of the octahedral or glassy forms in the presence of water or dilute sulphuric acid.

EXPERIMENTS TO DETERMINE MELTING POINT OF OCTAHEDRAL FORM.

The available data, however, permit of no conclusion as to the relationship of the two crystalline forms or as to what are their exact melting points. In the hope of obtaining more definite information on these points, some experiments were made by the writers of this paper, the results of which are briefly stated here.

In four experiments, arsenic trioxide was sublimed in an evacuated tube, the temperature being about 300° C. in the end containing the material and uniformly decreasing to 220° C. at the other end. In every test octahedral crystals formed in that part of the tube where the temperature was below 255° C.±5° C. No monoclinic crystals were obtained, but below this point for some distance the arsenic trioxide vapor condensed to a liquid, which solidified to the glassy form on cooling the tube. The melting point of the octahedral crystals, therefore, is not higher than about 255° C.

An attempt was made to determine this point more exactly by observing with the microscope small crystals contained in flat capillary tubes as the temperature was gradually raised. The experiment was conducted in a vapor bath similar to that used for the vapor-pressure determinations, the temperature being varied by changing the pressure above the boiling liquid. It was found, however, that the actual melting point could not be determined visually because the high viscosity of the fused arsenic trioxide obscured the melting point.

The usual method of melting-point determination by thermal analysis was also tried, using very fine copper-constantan thermoelements. The heating curve plotted from the results showed only a slight flattening in the region of 250° to 255° C., indicating that the heat of fusion is small.

As a final expedient, a series of small tubes, each containing a single well-formed octahedral crystal, was heated for three or four hours at temperatures ranging from 250° to 256° C. and the crystal subsequently examined under the microscope for evidence of fusion. From the results of these experiments, which will not be presented in detail, the melting point of the octahedral modification is provisionally set at 251° C.±1° C.

TRANSFORMATION TO MONOCLINIC FORM.

As regards the formation of the monoclinic modification, it was found that when octahedral crystals were fused in a capillary tube which had been thoroughly evacuated with the mercury pump, and the resulting fusion kept at any temperature between the melting

point and approximately 300° C., recrystallization began, usually in the course of half an hour. Star-like masses of crystals having the power to rotate polarized light developed very slowly, but the complete transformation was a matter of days. The form of these crystals corresponded in general to that of those described by Dana[a] for the mineral claudetite. When octahedral crystals contained in dry evacuated capillary tubes were held in a naphthaline vapor bath at 218° C. there was no transformation at the end of several days, although eventually the monoclinic crystals appeared and grew slowly. The extreme sluggishness of this change is illustrated by an experiment with a single octahedral crystal of 0.1 to 0.2 mm. diameter. The crystal had not completely disappeared when kept for two weeks in an evacuated capillary tube containing monoclinic crystals.

There is indeed a striking contrast between the slow formation and growth of monoclinic crystals and the facility with which octahedral crystals appear. In the experiments just referred to, the octahedral material, no doubt because of slight inequality of temperature, often shifted its position in the tube from hour to hour, appearing sometimes as a single large crystal, sometimes as a group of small crystals, but nothing of this sort was ever observed with the monoclinic allotrope. It is interesting to note that under the conditions just considered the transformation in situ of octahedral to monoclinic crystals was not observed.

The rate of transformation is greatly increased when a small quantity of water is sealed in the tube with the octahedral material. Under these conditions the time required to complete the process, at 218° C. with crystals 0.1 to 0.2 mm. in diameter, becomes a matter of minutes instead of days. On the other hand, the rate of transformation at this temperature, when in contact with the ordinary atmosphere, of roughly 60 per cent humidity, is only a little greater than that in the complete absence of air and water vapor. The change from octahedral to monoclinic crystals was also observed after several hours' heating at 100° C. in the presence of water or dilute or concentrated sulphuric acid. In an attempt to obtain this transformation at a lower temperature minute capillary tubes containing an intimate mixture of both kinds of crystals of 0.01 to 0.03 mm. diameter and a saturated solution of octahedral crystals in either water or dilute sulphuric acid were kept in the laboratory at room temperature for several months. At the end of this period no indication of the growth of either form at the expense of the other could be observed. It appears, therefore, that the monoclinic form is the stable one at temperatures above 100° C. and possibly even at room temperature. In fact, there is nothing to show that the transformation from octahedral to monoclinic is not monotropic—that is, irreversible.

[a] Dana, J. D., A system of mineralogy. 1911, p. 199.

MELTING POINT OF MONOCLINIC FORM.

The melting point of the monoclinic form was determined by the methods first employed with the octahedral form, using mercury as the boiling liquid, and was found to be approximately 313° C. As with the octahedral modification, the fusion was decidedly sluggish and the melting point was not as sharp as could be desired. The presence of moisture lowers the melting point decidedly.

The octahedral material used was prepared by subliming Baker's C. P. As_2O_3 at least once and from the sublimed trioxide the monoclinic crystals used for the melting point determinations were made. This material was not tested for impurities, but it is not likely that any were present in sufficient quantity to seriously influence the results. All temperature measurements were made with copper-constantan thermoelements calibrated at the boiling points of water, naphthaline, and benzophenone.

GENERAL CONCLUSIONS.

As regards the vapor pressure determinations it is evident that the octahedral modification is unstable throughout the entire temperature range investigated. When, however, we take into consideration the relatively large quantity of octahedral material used and the short duration of the experiments as compared with the slowness of the transformation to the monoclinic form it appears highly probable that the original substance was at all times present in sufficient quantity to saturate fully the passing air.

It seems safe to conclude, therefore, that the vapor pressures determined between 100° and 251° C. correspond to the vapor pressures of the unstable octahedral modification and that the two determinations above that temperature (Nos. 64, 65, Table 1) and those of Stelzner (Table 2) apply to the fused material. The absence of any sudden change in the values of the vapor pressure or heat of evaporation above 251° C. is not surprising in view of the apparent low heat of fusion and the fact that the liquid phase formed is also unstable at temperatures below the melting point of the monoclinic form. The vapor pressure of the monoclinic allotrope within its range of stability would of course be lower than that of any unstable modification.

VAPOR PRESSURE OF ARSENICAL FLUE DUST.

RECORD OF EXPERIMENTS.

Some preliminary determinations of the vapor pressure of a sample of fairly typical flue dust, containing 31.4 per cent arsenic trioxide, from the main dust chamber of a large copper smelter yielded distinctly lower values than those obtained from pure arsenic trioxide. This result was quite unexpected, and as it raised a question of

much importance, a series of determinations was made for the temperature range frequently found in smelter flues near the stack base. The method and apparatus employed were the same as those used in the preceding work. The results appear in Table 5, as follows:

TABLE 5.—*Summary of the flue-dust experiments.*

Experiment No.	Temperature.	Volume of air, based at 0° C. and 760 mm.	As_2O_3.	Vapor pressure.	Experiment No.	Temperature.	Volume of air, based at 0° C. and 760 mm.	As_2O_3.	Vapor pressure.
	°C.		Grams.	Mm.		°C.		Grams.	Mm.
1	181.0	1.880	0.00376	0.086	20	198.0	1.882	0.01128	0.258
2	180.5	1.873	.00529	.122	21	200.0	1.880	.01450	.332
3	180.6	1.873	.00624	.143	22	200.0	1.891	.01442	.328
4	180.4	1.869	.00572	.132	23	200.0	1.886	.01513	.344
5	180.5	1.869	.00526	.121	24	200.0	1.878	.01684	.386
6	180.6	1.871	.00452	.104	25	200.0	1.888	.01699	.386
7	181.0	1.882	.00471	.108	26	205.0	1.876	.01790	.410
8	181.0	1.871	.00453	.104	27	205.0	1.889	.01899	.432
9	181.0	1.892	.00508	.116	28	205.5	1.876	.01858	.426
10	185.0	1.878	.00495	.113	29	205.5	1.874	.01875	.430
11	185.0	1.874	.00531	.122	30	204.5	1.890	.01976	.449
12	185.0	1.896	.00542	.123	31	215.0	1.871	.02931	.674
13	185.0	1.895	.00415	.094	32	213.5	1.876	.02632	.603
14	190.0	1.885	.00754	.171	33	215.0	1.870	.02790	.641
15	191.0	1.892	.00930	.211	34	218.0	1.870	.03410	.784
16	190.0	1.889	.00877	.200	35	218.0	1.879	.03754	.858
17	195.0	1.881	.01017	.232	36	217.0	1.904	.0340	.768
18	195.0	1.892	.01117	.254	37	218.0	1.874	.0417	.957
19	194.0	1.879	.01009	.231					

For comparative purposes these results are presented graphically in figure 2, with the vapor-pressure curve for pure arsenic trioxide, drawn from the data presented in Table 3.

DISCUSSION OF LOW VALUES FOR VAPOR PRESSURE OF FLUE DUST.

The vapor pressure of the flue dust is seen to be, roughly, half that of the pure material. The indication of the preliminary experiments is thus confirmed, but the magnitude of the difference in the vapor pressure was a decided surprise, in view of the high percentage of As_2O_3 carried by the dust, and the conclusions deducible are rather far-reaching. In the first place, it is to be noted that this low value for the vapor pressure at once precludes the presence of the octahedral modification of arsenic trioxide in the flue dust, for if only a small part of the total arsenic were present in this form mechanically mixed with other compounds the material would still show the normal vapor pressure of this pure substance.

In seeking an explanation one must therefore consider carefully the mode of occurrence of the arsenic in the flue dust. Two possibilities suggest themselves: (1) The arsenic trioxide may either be present in some allotropic form having a lower vapor pressure than the octahedral modification, or (2) in solid solution, or in chemical combination with other substances present, in which case the observed vapor pressure values represent the partial pressure or dissociation pressure of arsenic trioxide from one or more of the solid phases.

As to the first possibility, the preliminary investigation of the crystalline modifications of arsenic trioxide, previously discussed, shows that throughout the range of temperature covered by the flue-dust experiment there is a form of the substance—the monoclinic—

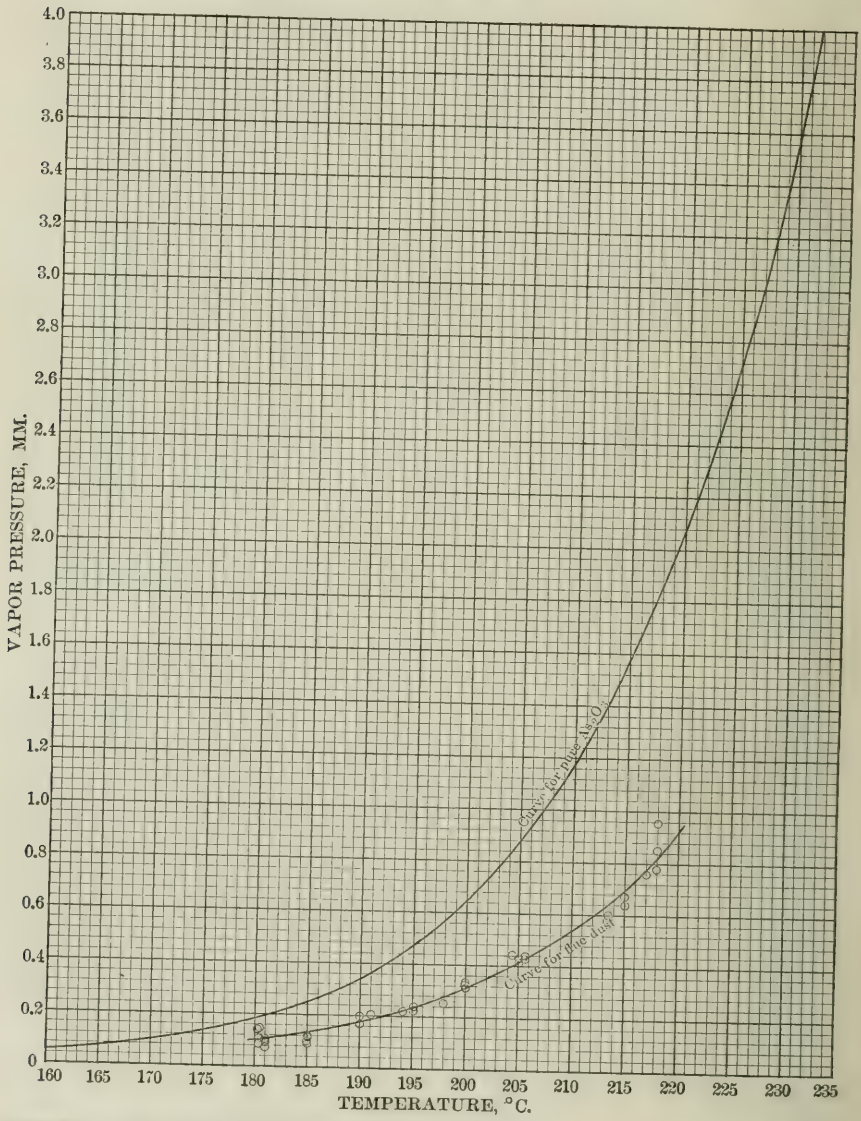


FIGURE 2.—Curves showing vapor pressures of arsenical dust and of pure arsenic trioxide at different temperatures.

which, because it is the stable form, must have the minimum vapor pressure. Moreover, if it be assumed that the arsenic trioxide vapor in the flue gases originally condenses to form octahedral crystals, the conditions in the flue—namely, a temperature of about 200° C. and

the presence of sulphuric acid—are excellent for the rapid transformation into the more stable form. Until the vapor pressure of the monoclinic modification has been accurately determined, no conclusion can be reached as to the correctness of the above explanation.

On the other hand, a number of considerations may be advanced in support of the idea that the arsenic trioxide is not present in the flue dust in the free state. In addition to the 31.4 per cent of arsenic trioxide, the dust contained zinc, lead, and other metals, probably as oxides, basic sulphates, or sulphates, small quantities of silica, metallic sulphides, and sufficient sulphuric acid to render the dust strongly hygroscopic. As is well known, arsenic trioxide has the characteristics of an amphoteric substance in that it forms compounds with both acids and bases. It also forms a variety of complex or molecular compounds,[a] and the presence in the flue dust of the larger number of substances noted above offers ample opportunity for such combinations to take place.

An observation made in carrying out the determinations of the vapor pressure of flue dust is of interest in this connection. The lower part of some of the deposits in the condensing tube was colored somewhat yellow or reddish, and on dissolving in concentrated hydrochloric acid a small yellow precipitate remained which was identified as arsenic trisulphide, but was not quantitatively determined. This occurrence suggested the possibility that the arsenic was present in the flue dust in some complex compound which also contained sulphur, and although definite proof of the existence of a specific compound is lacking, the idea is consistent both with the chemical character of arsenic trioxide and with the complex nature of flue dust. Further, the fact that the flue-dust determinations show a greater variability than those of pure arsenic trioxide suggest that a complicated and more or less variable solid phase was under investigation. Beyond these general suggestions no explanation of the low value of the vapor pressure can be given until the constitution of flue dust has been thoroughly investigated, and the results are quoted largely to point out the magnitude of the error that may be made in applying the data for pure octahedral As_2O_3 to actual flue conditions without first thoroughly investigating the details of the particular problem in hand.

PRACTICAL SIGNIFICANCE OF RESULTS.

The vapor-pressure determinations do, however, point to an approximate upper limit for the amount of arsenic trioxide carried by the gases in flues in which this type of flue dust prevails. Between 180° and 220° C. this quantity is not more than half that corresponding to vapor pressure of pure arsenic trioxide, and one would therefore expect pure arsenic trioxide to evaporate when subjected to the action

[a] Abegg, R. W. H., Handbuch der Anorganischen Chemie, Bd. 3, 1906, p. 519.

of the flue gases. Such evaporation was shown by lowering a weighed lump of pure octahedral arsenic trioxide into the flue, from which the dust was taken, adequate provision being made to protect the lump from the erosive action of the flue dust. In four days the loss was 9 per cent.

UNSATURATED CONDITION OF FLUE GAS.

Some further experiments in which flue gas at flue temperature was drawn through a thick layer of flue dust filtered from the gas at the point of experiment, showed that the arsenic content of the gas was increased by this treatment. In other words, the gas in the flue was not saturated even with respect to the flue dust which it carried. This condition probably resulted from the high velocity in the flue not allowing time for the establishment of equilibrium between the flue dust and the gas stream which was being continually diluted by air leaking through the flue walls, and particularly by gas partly deprived of its arsenic compounds by the chilling effect of the roof and sides of the flue.

GENERAL CONCLUSION.

In conclusion it may be said that although these results from the flue-dust experiments are largely of a qualitative character, they nevertheless show that the quantity of arsenic compounds, carried as vapor by the flue gas, is much less than would be expected from a knowledge of the vapor pressure of pure arsenic trioxide.

SUMMARY OF INVESTIGATION.

The investigation here reported may be summarized as follows:

A method has been developed for the accurate determination of the vapor pressure of solids for the temperatures at which vapor pressure is very slight; that is, from a few millimeters to less than 0.001 mm.

The vapor pressure of the octahedral modification of arsenic trioxide and, above 251° C., of the subcooled liquid have been determined at many points between 100° and 260° C., and by combination with other data, average values have been calculated for some temperatures between 100° and 300° C.

The heat of sublimation of arsenic trioxide has been computed for temperatures between 110° and 290° C.

The melting points of the octahedral and monoclinic modifications of arsenic trioxide have been determined to be approximately 251° C. and 313° C., respectively, and the monoclinic form has been shown to be the stable one for temperatures above 100° C.

Preliminary experiments with rather richly arsenical dust from the main flue of a copper smelter show that the arsenic trioxide vapor pressure exerted by it was only about half that exerted by the pure material.

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